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#### Formation of Sol Gel Dried Droplets of Carbon Doped Dioxide (TiO<sub>2</sub>) at Low Temperature Titanium via **Electrospraying**

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Abstract. The high band gap energy of  $TiO_2$  and inconsistency in particles size has imposed a significant drawback on TiO<sub>2</sub> applications. Dried droplets of carbon-doped TiO<sub>2</sub> fine particles were produced by using electrospraying technique. The C-doped TiO<sub>2</sub> particles were prepared by hydrolysis of titanium isopropoxide with the addition of carbon precursor followed by electrospraying the suspension in stable Taylor cone-jet mode. Coulomb fission of charged droplets from the electrospraying technique successfully transformed dispersed liquid C-doped TiO<sub>2</sub> particles into solid. The deposited C-doped TiO<sub>2</sub> droplets were collected on aluminium substrates placed at working distances of 10 to 20 cm from the tip of the electrospray needle. The collected C-doped TiO<sub>2</sub> droplets were characterized by using FESEM, UV-Vis, FTIR and XRD. By increasing the working distance, the average droplets size of the deposited C-doped  $TiO_2$  was reduced from ±163.2 nm to ±147.56 nm. UV-Vis analysis showed a strong absorption in the visible-light region and about 93 nm red shift of the onset spectrum for Cdoped  $TiO_2$ . The red shift indicates an increase in photocatalytic efficiency by reducing the TiO<sub>2</sub> band gap energy from 3.0 eV to 2.46 eV and shifting its activity to the visible-light region. FTIR analysis indicated the presence of Ti-C and C-O chemical bonding in the C-doped TiO<sub>2</sub>.

#### **1.** Introduction

Titanium dioxide  $(TiO_2)$  is a promising material that can be used in the degradation of pollutants due to its highly photosensitive, chemically stable, biologically inert and non-toxic in nature. Unfortunately, TiO<sub>2</sub> has a drawback which is high band gap energy (3.2eV) that is activated under ultraviolet light ( $\lambda < 387$ nm). The high band gap energy is due to oxygen vacancies and localization of Ti 3d states [1,2]. Other than that,  $TiO_2$  is also thermally unstable which leads to easy phase transformation [3], depending on its synthesis method. To improve  $TiO_2$  properties, methods need to be developed for controlling the droplet size, surface are and morphology, as well as doping with other elements to enhance the photochemical response of TiO<sub>2</sub> towards the visible-light region.

The properties of TiO<sub>2</sub> can be altered by doping, where an impurity is intentionally introduced into  $TiO_2$ . There are three opinion regarding the modification mechanism of the doped  $TiO_2$ . First is narrowing the TiO<sub>2</sub> bandgap by substituting oxygen in TiO<sub>2</sub> lattice [4], second, introducing an impurity energy level above the valence band [5], and lastly the formation of oxygen vacancy sites as blockers for reoxidation [6]. All three mechanisms lead to improvement of the TiO<sub>2</sub> properties. In this

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study, carbon element [7] is chosen as the doping element to produce C-doped TiO<sub>2</sub>. Carbon is a promising doping element due to its significant overlapping of electron state between the oxygen near the valence band of TiO<sub>2</sub> [8]. Carbon also has high adsorption capacity, it can be used in both air pollutant degradation and waste water treatment as well as five times more active than nitrogen and other doping element under visible-light irradiation [9]. Methods of producing TiO<sub>2</sub> also have been studied in order to produce C-doped TiO<sub>2</sub> with the desired particle size, morphology and structural characteristic.

Various methods have been used to produce C-doped  $\text{TiO}_2$  particles, such as chemical precipitation [10,11,12], sol-gel [13,14] and electrospray drying. In the chemical precipitation method, C-doped TiO<sub>2</sub> suspension needs to be heated rapidly for the hydrolysis process to occur. Precipitates need to be washed and then heated again to produce particles. As a result, the C-doped TiO<sub>2</sub> particles produced from this method are highly aggregated and lead to a wide distribution of particle sizes. In the sol gel method, control of the hydrolysis process is essential in order to obtain a homogenous oxide network. This requires long aging process to produce C-doped TiO<sub>2</sub> particles. As a result, the desired anatase phase of C-doped TiO<sub>2</sub> particles was difficult to obtain because of repetition of the heating process and the high calcination temperature. Besides, the produced C-doped TiO<sub>2</sub> also has inconsistent particle sizes due to the grinding process. Therefore, electrospraying technique is introduced in this study as a method to produce fine and uniform C-doped TiO<sub>2</sub> particles without heating at high temperature, aging or grinding process as required in other methods.

Electrospraying or electrohydrodynamic spraying is a method of liquid atomization by electrical forces [15]. It has the ability to produce monodisperse particles, reduce molecular aggregation and operated at ambient condition [16]. The size of the electrospray droplets ranges from hundreds of micrometers down to tens of nanometers. The droplets are highly charged up to a fraction of the Rayleigh limit, which is the maximum charge carried by a droplet. The charge will overcome the liquid surface tension and leads to fission of the droplets. Charged droplets are self-dispersing within the working distance due to the fission process, resulting in the absence of droplets agglomeration [17,18]. Therefore, the electrospraying technique is proposed in this study to produce visible light active C-doped  $TiO_2$  particles.

#### 2. Materials and Methods

#### 2.1 Preparation of C-doped TiO<sub>2</sub> suspension

C-doped TiO<sub>2</sub> suspension was prepared by adding titanium isopropoxide (TTIP) (98%, Sigma-Aldrich Chemie, GmBH) drop-wise as a precursor into 50 mL of deionized water. The mixture was stirred at 500 rpm under room temperature until it turned to cloudy yellow. The cloudy suspension was then dispersed into a mixture of 50 mL ethanol and 10 mL acetic acid (99%, Merck KGaA, Darmstad Germany). Different concentrations (0.25 M, 0.5 M, 0.75 M and 1.0 M) of acetylacetone (98%, Merck KGaA, Darmstad Germany) as a dopant precursor were added to the suspension. The suspension was stirred for 1 hour and sonicated (QSonica Sonicators, Q700) at amplitude of 50 kHz for 30 min. The same procedure was used to prepare the un-doped TiO<sub>2</sub> suspension by using TTIP.

#### 2.2 Electrospray deposition of C-doped TiO<sub>2</sub> suspension

Electrospray equipment was set up as shown in Figure 1. The prepared C-doped TiO<sub>2</sub> suspension was loaded into a 25 mL syringe with a needle size of 0.15 mm inside diameter on a syringe pump (SP-1000, Next Advance Inc). The needle tip and counter electrode were connected to an electrostatic generator (G60 EMCO High Voltage). An AC-DC converter (M10-QS305, MCP Lab Electronics) was used to convert alternate current to direct current before connecting it to the electrostatic generator. Positive and negative charge voltage was applied at the needle tip and counter electrode respectively. The flow rate of the C-doped TiO<sub>2</sub> suspension was set at 2.0 mL/h. Voltage was applied in a range of 1.23 to 1.28 kV to maintain the formation of a Taylor cone meniscus at the needle tip. Dispersed C-doped TiO<sub>2</sub> droplets were collected on a flat surface grounded substrate at various working distances (WD) of 10 cm, 15 cm and 20 cm from the counter electrode. The substrate containing deposited droplets were dried in an oven at 60-100 °C for 1 hour.



Figure 1. Electrospray setup and mechanism

#### 2.3 Estimation of primary charged droplet size

The primary charged droplet size of C-doped  $\text{TiO}_2$  can be estimated by using a scaling law to investigate the droplet fission behaviour of electrospraying, proposed by Hartman et al. [19] Equation (1), Fernandez de la Mora [20] Equation (2) and Ganan-Calvo [21] Equation (3) respectively, as follows:

$$d_d = \left(\frac{\rho \varepsilon_o Q^3}{\gamma K}\right)^{1/6} \tag{1}$$

$$d_d = 1.66\varepsilon_r^{-1/6} \left(\frac{Q\varepsilon_r \varepsilon_0}{\nu}\right)^{1/3}$$
(2)

$$d_d = 1.2164 \left(\frac{Q\varepsilon_F \varepsilon_O}{K}\right)^{1/3} \tag{3}$$

Where  $d_{d_p}$ ,  $\varepsilon_{o_p}$ , Q,  $\gamma$ , K and  $\varepsilon_r$  are the primary droplet size (m), liquid density (kg/m<sup>3</sup>), electrical permittivity of vacuum (C<sup>2</sup>/Nm), liquid flow rate (m<sup>3</sup>/s), surface tension (N/m), conductivity of liquid (S/m) and relative permittivity respectively. Assuming evaporation of droplets occurs without substantial loss of mass by any other mechanism during electrospaying, the theoretical dried droplet size ( $d_p$ ) can be calculated according to Equation (4).

$$d_p = d_d \theta^{1/3} \tag{4}$$

Where  $d_p$  is the theoretical dried droplet size and  $\theta$  is the volume fraction of material in the solution. The number of fission was determined by dividing the volume of primary charged droplet size over the volume of dried droplets from the diameter of the droplets size of FESEM images. The volume of the droplets is assumed to be spherical. The electrosprayed particles on the substrate were scraped out and characterized using Field Emission Scanning Electron Microscopy (FESEM), UV-Visible Spectroscopy (UV-Vis), Fourier Transform Infrared Spectroscopy (FTIR) and using X-Ray Diffraction (XRD). UV-Visible Spectroscopy (UV-Vis) was used to study the changes in absorption wavelength for both C-doped and un-doped TiO<sub>2</sub> samples. Absorbance data for all samples were recorded at wavelength. Fourier Transform Infrared Spectroscopy (FTIR) was used to study changes in functional group for the electrosprayed C-doped TiO<sub>2</sub> samples. The scan spectra were recorded in the range from 500 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. The crystal phase of the electrosprayed C-doped TiO<sub>2</sub> samples was performed at 40 kV and 150 mA at an angle of 2 $\theta$  from 20<sup>o</sup> to 80<sup>o</sup>. The scan speed was 1<sup>o</sup>/min.

### 3. Results and Discussion

Figure 2 shows the relationship between the zeta potential and particles size in suspensions with various pH. High zeta values were recorded at pH 2 and 13, at 27.98 mV and -45.65 mV respectively. The zeta potential is a term referring to the electrical potential at the boundary of a double layer of particles surface in suspension. Particle suspensions with zeta potential values approximately or closer to  $\pm 30$  mV have high degrees of stability [22]. In terms of the particle size in suspensions, at pH 2 and 13, small C-doped TiO<sub>2</sub> particles were obtained with an average size of 249.12 nm and 278.25 nm respectively. Prior to electrospraying, the C-doped TiO<sub>2</sub> suspension was stabilized at pH 2 because this is close to the suspension's initial pH of 3.2. In the acidic condition, the C-doped TiO<sub>2</sub> particles in suspension carried a positive charge as the H<sup>+</sup> ions surrounded its surface. This condition is similar to the initial condition of the suspension before acid was added to reduce the pH. Thus, only a little acid is required to add into the suspension.



Figure 2. Zeta potential and particles size in suspension versus pH

In this study, the isoelectric point obtained for the C-doped  $\text{TiO}_2$  suspension was at pH 4.3. Since no work was found for characterizing the zeta potential of C-doped  $\text{TiO}_2$  suspension, the isoelectric point for the C-doped  $\text{TiO}_2$  is referred to  $\text{TiO}_2$  suspension which has a pH range from 4.0 to 7 [23]. At the isoelectric point, H<sup>+</sup> and OH ions are neutralized and there is no charge surrounding the C-doped  $\text{TiO}_2$  particles surface. Therefore, C-doped  $\text{TiO}_2$  particles tend to flocculate due to the attractive Van der Walls force and later sedimentation occurred. As shown in Figure 2, at pH values near the isoelectric point, the biggest average particle size was recorded at 1088 nm. This is undesirable for C-doped  $\text{TiO}_2$  suspension to undergo electrospraying, because it is in an unstable condition. Hence, the C-doped  $\text{TiO}_2$  suspension was stabilized at pH 2 prior to electrospraying.

From Figure 3, morphological changes of the C-doped TiO<sub>2</sub> droplets were observed as the working distance (WD) was varied from 10 cm to 20 cm. A wide distribution of dried droplets ranging from 20 to 640 nm with average droplets size of 163.2 nm was observed at 10 cm WD. The droplets size distribution decreased to 20-500 nm and 20-360 nm for WDs of 15 and 20 cm with average droplets size of 162.9 and 147.6 nm respectively. Large C-doped TiO<sub>2</sub> droplets were collected at WDs of 10 cm and 15 cm, which indicated that less fission of primary charged droplets had occurred. The sizes of primary charged droplet, the deposited droplet size and numbers of fission events were estimated and shown in Table 1. Table 2 shows the numbers of fission that occurred during electrospraying increases when the WD increases from 10 cm to 20 cm for each of the scaling law models. From the experimental number of fissions, the number of fission is high for large size of primary charged droplet in agreement with the Fernandez de la Mora model [24], since the conductivity value of C-doped  $TiO_2$  suspension was sufficiently high (i.e. 0.8 S/m) which near to high conductivity condition as in the proposed model. The number of fission from the experiment is in agreement with theoretical number of fission calculated using Fernandez de la Mora model, equation (2). Where the number of fission value at the furthest distance is the closest to the theoretical results derived for the conductivity solution by Fernandez de la Mora [25].



**Figure 3**. FESEM images and droplets size distribution of deposited 0.5 M C-doped TiO<sub>2</sub> droplets at various WD. (a) 10 cm, (b) 15 cm (c) 20 cm

With increase in WD, the droplets have longer flight and solvent evaporation times, and thus have more time for fission to occur. Hence, this leads to the production of smaller average droplets size. Coulomb fission or explosion of droplets occurs when charged droplets reach the Rayleigh limit. The Rayleigh limit is the maximum amount of charge that a droplet can carry on its surface [26]. When the droplet reaches the Rayleigh limit, it becomes unstable because of the high density of charge on its surface and it breaks up into smaller droplets. The loss of mass during fission is too small to affect the droplet size [27]. The mechanism of Coulomb fission during electrospraying ensure the primary charged droplet underwent fission along the WD before deposited on the substrate [25, 38]. Hence, electrospraying technique could produce a narrow distribution of C-doped TiO<sub>2</sub> droplets with an average droplets size of 147 nm.

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<b>Table 1.</b> Estimation of primary and deposited droplets sizes.						
Scaling law model	Primary droplet	Theoretica	al deposited droplets	Theoretical number of		
	size, d <sub>d</sub> (nm)	size, d <sub>p</sub>	from Equation (4)	fission		
			(nm)			
Hartman	2755	642.83		79.02		
Fernandez de la Mora	641.46	149.67		79.79		
Ganan-Calvo	991.32	231.31		79.03		
Table 2. Estimation of experimental number of fission.						
Scaling law model	Expe	rimental	Experimental	Experimental		
	number	of fission,	number of fission,	number of fission,		
	WD =	= 10 cm	WD = 15 cm	WD = 20 cm		
Hartman	4	811	4837	6503		
Fernandez de la Mora		61	61	82		
Ganan-Calvo		224	225	303		
Average particle size, *	$d_p(nm)$ 10	53.2	162.9	147.6		

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c

**n** ...

\*d<sub>p</sub> is average deposited droplets size from FESEM image of the respective working distance (WD)

UV-Vis analysis of C-doped samples was performed, and the absorbance spectrum was obtained as shown in Figure 4. The cut-off wavelength for the un-doped TiO<sub>2</sub> sample was ~413 nm with calculated band gap energy of 3.0 eV. The absorbance spectrum for un-doped TiO<sub>2</sub> corresponded well with the anatase phase TiO<sub>2</sub> absorbance spectrum from previous work, which has a band gap energy of ~3.2 eV [28,29]. For the C-doped TiO<sub>2</sub> samples, the absorption spectrum was red-shifted and the cut-off wavelength was found at 420, 506, 493 and 440 nm for different dopant concentrations of 0.25, 0.5, 0.75 and 1.0 M respectively. An increase in the cut-off wavelength in this study, clearly indicated a decrease in the band gap energy for C-doped TiO<sub>2</sub> samples [30]. The band gap energy can be calculated from the UV-Vis absorbance spectrum and the relation between the band gap energy and cut-off wavelength in the absorption spectra is shown in Equation (5) [31]:

Band gap energy 
$$(E_{bg}) = \frac{hC}{\lambda}$$
 (5)

where h is Plancks constant (6.626 x  $10^{-34}$  Js), C is the speed of light (3.0 x  $10^8$  m/s),  $\lambda$  is the cut-off wavelength of UV-Vis spectra (m) and the conversion factor is 1 eV which is equal to 1.6 x  $10^{-19}$  J. The calculated band gap energy for doped TiO<sub>2</sub> is shown in Table 3.



From Table 3, it is observed that the band gap energy of C-doped TiO2 is lower than the un-doped TiO2. The presence of carbon in C-doped TiO2 samples creates interface states which result in low band gap energy of TiO2 [32]. The 0.5 M electrosprayed C-doped TiO2 has the lowest band gap energy compared to other electrosprayed C-doped TiO2 samples, which is 2.46 eV. The lowest band gap energy confirms that 0.5 M electrosprayed C-doped TiO2 has the best properties to be used as photo-catalyst and able to degrade pollutant faster under visible light. The observed variation of the

cut-off wavelength and the pattern of band gap energy depend on the carbon content in the C-doped TiO2 with varying dopant concentrations. This is because accommodation for carbon substitution in the TiO2 was limited when the dopant concentration increased. At high dopant concentration which is more than 0.5 M, excess of carbon presents in the samples. The excess carbon in doped TiO2 might hinder the excitation of electron from valence band to conduction band when the C-doped TiO2 irradiated under visible light.

Table 3. Band gap energy for un-doped and C-doped TiO<sub>2</sub> sample at different concentration

Sample	Cut off wavelength	$E_{bg}(J)$	$E_{bg}(eV)$
	(m)		
Un-doped electrosprayed TiO <sub>2</sub>	4.13 x 10 <sup>-7</sup>	4.81 x 10 <sup>-19</sup>	3.00
0.25M electrosprayed C-doped TiO <sub>2</sub>	4.2 x 10 <sup>-7</sup>	4.73 x 10 <sup>-19</sup>	2.96
0.5M electrosprayed C-doped TiO <sub>2</sub>	5.06 x 10 <sup>-7</sup>	3.93 x 10 <sup>-19</sup>	2.46
0.75M electrosprayed C-doped TiO <sub>2</sub>	4.93 x 10 <sup>-7</sup>	4.03 x 10 <sup>-19</sup>	2.52
1.0M electrosprayed C-doped TiO <sub>2</sub>	4.4 x 10 <sup>-7</sup>	4.52 x 10 <sup>-19</sup>	2.83
0.5 M un-electrosprayed C-doped TiO <sub>2</sub>	4.3 x 10 <sup>-7</sup>	4.62 x 10 <sup>-19</sup>	2.89

Hence, the excess carbon in the 0.75 M and 1.0 M electrosprayed C-doped caused high band gap energy. In summary, carbon in  $TiO_2$  acts as an impurity to form interface states that effectively lower the band gap. As for the 0.5 M unelectrosprayed C-doped  $TiO_2$  sample, the band gap energy obtained is 2.89 eV and the band gap is higher than for the 0.5 M electrosprayed C-doped  $TiO_2$ . As discussed earlier, electrosprayed C-doped  $TiO_2$  has a narrow distribution of fined-sized droplets and its high surface area provided more active sites. Hence, the efficiency of electrosprayed C-doped  $TiO_2$  under visible-light irradiation is increased.



**Figure 5.** FTIR results for C-doped  $TiO_2$  samples at different dopant concentration. (a) undoped  $TiO_2$ , (b) 0.5M unelectrosprayed C-doped  $TiO_2$ , (c) 0.5 M electrosprayed C-doped  $TiO_2$ 

The bonding characteristics of the functional groups in the C-doped TiO<sub>2</sub> samples were identified using FTIR. Figure 5 shows the absorption peaks for un-doped and doped TiO<sub>2</sub> samples. New strong peaks were formed for all the doped TiO<sub>2</sub> samples at around 1044.5, 1263.8, 1650 and 3387 cm<sup>-1</sup> [33]. Two peaks at 1044.5 cm<sup>-1</sup> and 1263.8 cm<sup>-1</sup> represent Ti-C and C-O bonds respectively. The peaks around 1650 cm<sup>-1</sup> and 3387 cm<sup>-1</sup> represent stretching vibration of OH bonds from surface water molecules and hydroxyl groups in the samples. In the photocatalytic mechanism, hydroxyl groups were trapped in holes that were generated when TiO<sub>2</sub> was irradiated under light. The hydroxyl radicals formed can suppress the recombination of electron-holes [34]. Therefore, the presence of carbon bonding and hydroxyl groups in electrosprayed C-doped TiO<sub>2</sub> shows the improvement in TiO<sub>2</sub> properties.



**Figure 6**: XRD pattern for C-doped TiO<sub>2</sub> samples. (a) undoped electrosprayed TiO<sub>2</sub>, (b) 0.5 M electrosprayed C-doped TiO<sub>2</sub> (c) 0.5 M unelectrosprayed C-doped TiO<sub>2</sub>

Figure 6 shows the crystalline phase of electrosprayed C-doped  $TiO_2$ . Only anatase phase was present in the C-doped TiO<sub>2</sub> at a diffraction angle of  $23^{\circ}$ ,  $37.6^{\circ}$ ,  $48^{\circ}$  and  $54^{\circ}$  [35]. No signals of rutile and brookite phase were detected. The presence of carbon as a doping element in  $TiO_2$  does not induce new crystalline forms other than anatase phase [36]. Acetylacetone used as a source of carbon doping is an organic compound to chelate the titanium atoms and is also responsible for the formation of anatase phase. The intensity of the anatase phase for both 0.5 M electrosprayed and unelectrosprayed C-doped TiO<sub>2</sub> was lower than the un-doped TiO<sub>2</sub>. This could be due to the low crystalline nature of the carbon element compared to titanium [37]. The reduced intensity of the anatase phase in 0.5 M Cdoped TiO<sub>2</sub> is a sign of the presence of carbon in the TiO<sub>2</sub> lattice. However, the peak and intensity of anatase for the un-electrosprayed 0.5 M C-doped TiO<sub>2</sub> was weak compared to the electrosprayed sample. In the electrospraying technique, the produced C-doped TiO<sub>2</sub> particles were dried properly, since the mechanism of droplet fission from electrospraying has been proven to facilitate solvent evaporation, so that only dried 0.5 M C-doped TiO<sub>2</sub> particles were collected. For the un-electrosprayed 0.5 M C-doped TiO<sub>2</sub>, the presence of impurities may cause the weak anatase peak formation in the XRD results. Hence, a high drying temperature or calcination process was needed for the unelectrosprayed 0.5 M C-doped TiO<sub>2</sub> to enhance the formation of the anatase phase.

#### 4. Conclusions

This work demonstrated that the TiO<sub>2</sub> suspension is most stable at pH 2, at which it has a high zeta potential and small particles size in suspension, which is 27.98 mV and 249.12 nm. A stable condition was crucial prior to electrospraying in order to avoid sedimentation of particles during the process. The direct current (DC) voltage applied in the electrospraying method can produce small size droplets with a narrow size distribution and an average droplets size of  $\pm 147.56$  nm. Increasing the distance from the needle tip to the substrate from 10 cm to 20 cm significantly reduces the deposited droplets size droplets with a narrow size distribution. The fission mechanism was utilized for drying and produces small size droplets with a narrow size distribution. Heating at low temperature was applied for doping the TiO<sub>2</sub> with carbon helps to improve the TiO<sub>2</sub> properties. It lowers the TiO<sub>2</sub> band gap to 2.46 eV and it can be activated under visible-light illumination.

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